

## SOLUBILITY OF GASEOUS HYDROCARBONS IN AQUEOUS SOLUTIONS: INITIAL MECHANISM FOR PROPANE ADSORPTION ON PLATINUM

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Early methods for the determination of gaseous hydrocarbon solubility in aqueous solution were based on static techniques.<sup>1,2</sup> Basically, the static technique involves bringing together an excess volume of gas and a measured quantity of gas-free solvent in an equilibrium cell, which is rocked for several hours to attain gas-solution equilibrium. Subsequent removal of the dissolved gas by manometric techniques,<sup>3</sup> however, appears to lack precision and becomes unwieldy. Therefore methods for hydrocarbon solubility determinations<sup>4,5</sup> were developed which applied inert gas-stripping techniques to isolated samples of gaseous hydrocarbon-saturated solutions. Collection of the stripped gaseous hydrocarbons was made on various adsorbents at reduced temperature ( $-80^{\circ}\text{C}$ ). The hydrocarbons subsequent release was effected by raising the temperature allowing the sample to be swept into a gas-liquid chromatograph (GLC). This GLC technique as developed by Swinnerton and Linneboom was found satisfactory for measurement of trace quantities of gas dissolved in solution, however, a desirable gas-saturation chamber was lacking. Thus it was necessary to develop a new dynamic method for gas-saturating aqueous solutions (electrolytes) which simulates gas-saturation as it exists in fuel cells. The technique described herein is being used to determine solubilities of gaseous hydrocarbons (propane) in the following fuel cell electrolytes: perchloric, sulfuric, phosphoric, and trifluoroacetic acids at 1 molar concentrations. Solubilities of propane in these electrolytes were used in conjunction with propane adsorption rate data obtained through linear anodic sweeps<sup>6</sup> to elucidate the mechanism of initial propane adsorption on smooth platinum.

EXPERIMENTAL

A Hewlett-Packard Model 5750 gas chromatograph equipped with dual flame ionization and thermal conductivity detectors was used. A six foot column packed with Chromosorb W coated with diisodecyl phthalate was used for the analysis and helium was employed as carrier gas. Research grade propane (99.9 mole percent) was obtained from Phillips Petroleum Company. The apparatus for propane saturation of electrolyte and subsequent collection of dissolved propane is shown in Fig. 1.

Propane is first humidified by passing through a glass-jacketed scrubber (A) having the same electrolyte and temperature as the test solution. The humidified propane bubbles through a jacketed vessel (B) effecting saturation of the electrolyte (150 ml). The gas train continues through line D and 3-way valves 1 and 2 to a 104 ml jacketed saturation-stripping chamber (E) containing 84 mls of electrolyte. Thus, a volume corresponding to 20 ml is reserved for propane during transit. All gas flow rates are measured and adjusted using a bubble flow meter. Excess propane exits from this chamber via 3-way valve 3 and 2-way valve 4 into a waste trap. The propane saturation process requires 30 minutes at a flow rate of 2.5 cc per second. Then 3-way valve 1 is turned to allow propane saturated electrolyte from vessel B to flow into the saturation-stripping chamber (E) via line C until it becomes filled. As soon as this is accomplished, 3-way valves 2 and 3 are closed simultaneously, to seal the saturation-stripping chamber. To purge outer line F of propane humidified helium is passed through line G and valves 3 and 4 before sample collection begins. Thirty minutes of helium purge is required to clear

line F of propane. To collect the sample 2-way valves 4 and 5, 3-way valves 2 and 3 and 2-way valve 6 are turned to allow humidified helium to strip the dissolved propane from the 104 ml chamber (E), the gas flows through line F, valve 5, drying tubes of magnesium perchlorate, and valve 6 into a closed test tube containing 5 mls of purified toluene maintained at  $-80^{\circ}\text{C}$ . Stripping and collection of propane requires 30 minutes. The test tube of toluene is then removed from the gas train, capped, and brought to room temperature. A 10 microliter aliquot sample is removed and injected via hypodermic syringe into the gas-liquid chromatograph. Before the next propane saturation run, 3-way valve 2, and 2-way valve 7 are turned to allow the electrolyte-filled chamber (E) to drain to starting level of 84 ml.

### CALIBRATION

The Hewlett-Packard gas chromatograph Model 5750 used in this work is equipped with a Mosley Recorder and a Disc Integrator Model 229 to record and integrate peak area. Propane retention time is 0.4 minutes at a column temperature of  $89^{\circ}\text{C}$  and a helium carrier gas flow rate of 20 cc per min. The chart speed was one inch per minute. To calibrate the gas chromatograph 20 microliter of pure propane gas was injected using a Hamilton gas-tight syringe. The number of integrator counts was recorded and used as a standard. Since the ratio of area to volume for the standard is directly proportional to the area-volume ratio of the sample the quantity of propane in the sample was calculated.

The technique<sup>6</sup> employed to obtain data on the rate of propane adsorption at a smooth platinum electrode was a modified version of the multipulse potentiodynamic (MPP) sequence with a linear anodic sweep (las) of 10 volts per second. This sequence allows measurement of charge required to completely strip the propane adsorbed at the study potential at various times. This is accomplished by subjecting the anode to the MPP sequence in presence, first of helium and then propane. The charge obtained with helium,  $Q_{\text{He}}$ , is subtracted from that in the presence of propane,  $Q_{\text{p}}$ , to obtain the desired charge difference  $\Delta Q$ . The duration of the study potential step was identical for both  $Q_{\text{He}}$  and  $Q_{\text{p}}$  measurements.

### RESULTS AND DISCUSSION

In these experiments the molarity of the acid was considered constant. Using this basis a series of results relating the mole fraction of dissolved propane to temperature are shown (Fig. 2). Both 0.5 and 1.0 molar sulfuric acid solutions have approximately the same solubility within the conditions of the experiment; thus, indicating that in this example ionic concentrations do not substantially interfere with the solubility of propane. Another interesting feature concerning this acid is that the quantity of dissolved gas does not vary with temperature between  $20^{\circ}$  and  $65^{\circ}\text{C}$ .

However, in examining the solubility data for the other acids one finds a similarity between the phenomena displayed in water as a function of temperature and that in perchloric, trifluoroacetic, and phosphoric acids. In these data one finds that at  $65^{\circ}\text{C}$  the solubility of propane in all the acids and in water is the same quantity within the precision of the experiments. At lower temperatures a difference in the quantity of dissolved gas was observed. For example, at  $40^{\circ}\text{C}$  an appreciable difference has been measured. At  $20^{\circ}\text{C}$  the propane gas is now adsorbed in the largest quantity in water while the amount in the acid solutions has some dependence on the character of the acid. Figure 2 also illustrates the anomalous behavior<sup>7</sup> of water in which a maximum propane solubility is observed. Similar behavior is displayed in all the acids examined with the exception of sulfuric. The degree of hydration associated with sulfuric acid may account for this invariant behavior for propane solubility at these temperatures.

The solubility data once obtained can be used in making certain statements concerning the initial process of propane adsorption on a smooth platinum surface measured by linear anodic sweeps. If semi-infinite linear diffusion is assumed, the rate of accumulation of charge is given by<sup>8</sup>

$$Q = 2nF \frac{D}{\pi}^{\frac{1}{2}} C_{C_3H_8} t^{\frac{1}{2}}$$

The symbols have their usual significance. Although it has been previously shown<sup>9</sup> that the overall oxidation of propane to carbon dioxide and water involves 20 electrons, it has been determined that using las techniques  $n$  should be equal to 17 electrons<sup>10</sup> since three hydrogen atoms are lost upon adsorption at potentials equal to or greater than 0.3 volts. Therefore, using the measured values of propane dissolved in solution we may calculate from the linear portions of Figs. 3 and 4 the diffusivity of propane in perchloric acid as  $0.156(10^{-8}) \text{ cm}^2 \text{ sec}^{-1}$  and in sulfuric acid as  $0.067(10^{-8}) \text{ cm}^2 \text{ sec}^{-1}$ . These calculations are in agreement with the approximate inverse relationship of diffusivity and viscosity. In Fig. 5 one can see that the viscosity of perchloric is less than that of sulfuric acid.

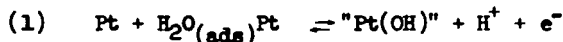
Another interesting phenomenon which seems evident is the change in slope (Fig. 4) as a function of potential in perchloric acid. These apparent deviations are observed at times of one second and are in contrast with the diffusion-limited process portrayed in sulfuric acid (Fig. 3) as a function of potential. In sulfuric acid the initial adsorption is diffusion-controlled for approximately 60 seconds at 0.2 and 0.3 volts while deviations from linearity occur after 8 seconds at 0.4 volts. These times are in general agreement with observations of Brummer<sup>10</sup> in concentrated phosphoric acid.

Further consideration of the data at anodic potentials of 0.3 and 0.4 volts is shown in Fig. 6. Here, in the perchloric acid anion environment propane adsorption can be described by

$$Q = A + B \log t$$

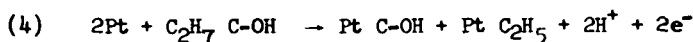
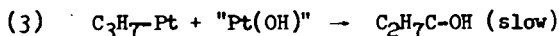
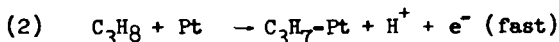
in which  $Q$ =charge per  $\text{cm}^2$ ,  $t$ =time, and  $A$  and  $B$  are parameters which depend on the type of adsorption occurring. This relationship continues until a time invariant condition is achieved on the platinum surface. Since this difference in behavior in the two acids has already been found not to be a function of the propane concentration, other possible explanations are considered.

It has already been postulated<sup>11</sup> that at potentials less anodic than reversible oxygen the electrochemical formation of "O" type species from the electrolyte may proceed via the mechanism



This type of reaction, of course, will proceed at an electrode surface at which the least specific anion adsorption occurs. Since, perchloric acid anions are less adsorbed than sulfate the rate of formation of the partially oxygenated species on platinum will proceed at a faster rate due to the concentration of  $\text{H}_2\text{O}$  at the interface. Evidence of decreased perchloric anion adsorption has already been presented by some of the authors.<sup>6</sup> Here it was shown that the total propane adsorbate

was greater in perchloric acid indicating it has a lesser degree of anion coverage. Since reaction (1) then occurs it is possible that at 0.3 volts in very short times some of the adsorbed species may undergo this mechanism



Similar type mechanisms<sup>12,13</sup> have been suggested, but the possibility of reaction (1) occurring is made more evident by the work of Hunger.<sup>14</sup> This postulated mechanism demonstrates a curious position. For in perchloric acid as compared to sulfuric the competition of anions for active sites decreases, hence the degree of partial oxygenation of platinum increases. With this condition, O-type hydrocarbon species are formed and the carbon-carbon bonds are more easily broken. Therefore, the amount of available sites decreases and the rate of further deposition becomes adsorption-controlled at these low anodic potentials. In contrast, the diffusion controlled mechanism in sulfuric acid may indicate the lack of surface reactions and subsequent increase in surface coverage due to the formation of free radicals and oxygenated species originating from propane at the potentials studied. Interestingly enough, the adsorption of methanol,<sup>15</sup> a partially oxygenated compound, also follows an adsorption isotherm.

#### CONCLUSIONS

The solubility of propane seems to be about the same in the electrolytes studied. Thus, the initial rate of propane adsorption is influenced by surface conditions at the platinum anode. The tendency of the anion to specifically adsorb and the rate of partial oxidation of the platinum surface seem to be interrelated factors which dictate the initial mechanism of propane adsorption.

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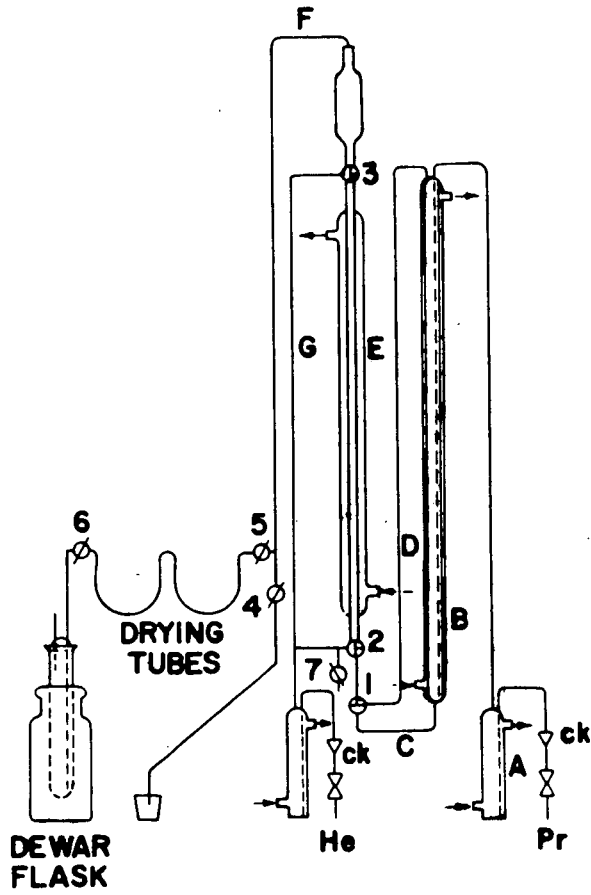


Fig. 1

## GAS SOLUBILITY APPARATUS

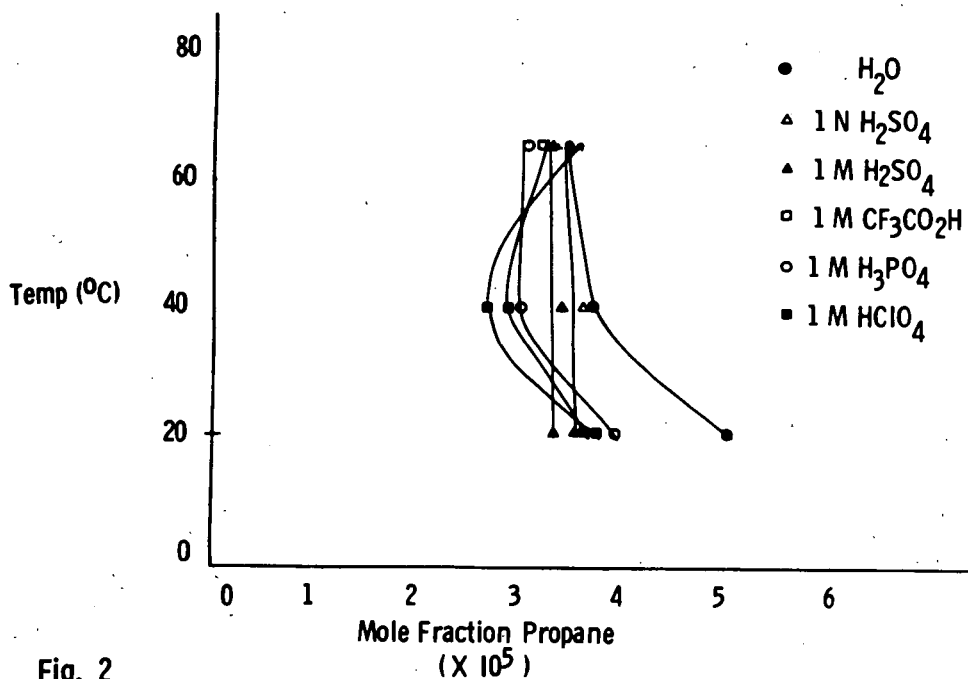


Fig. 2

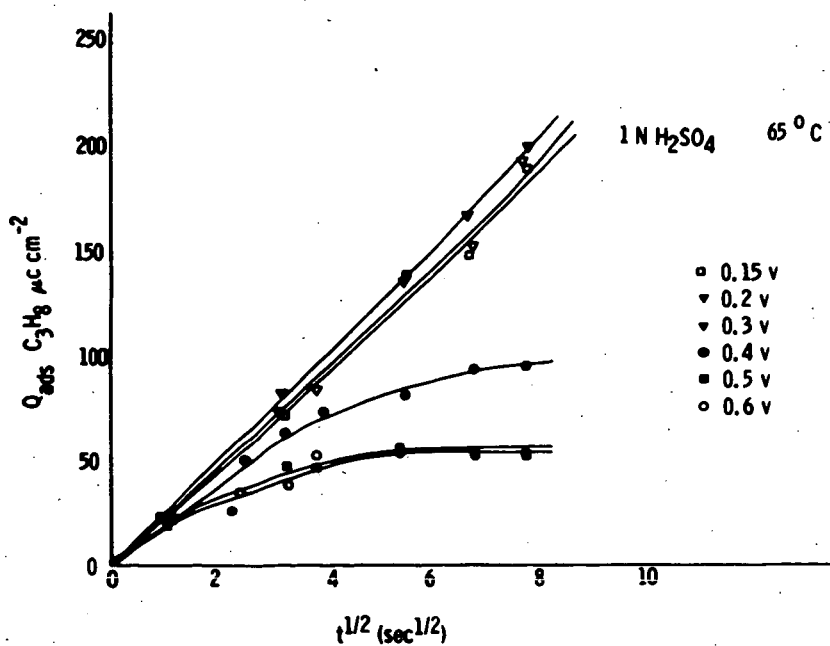


Fig. 3

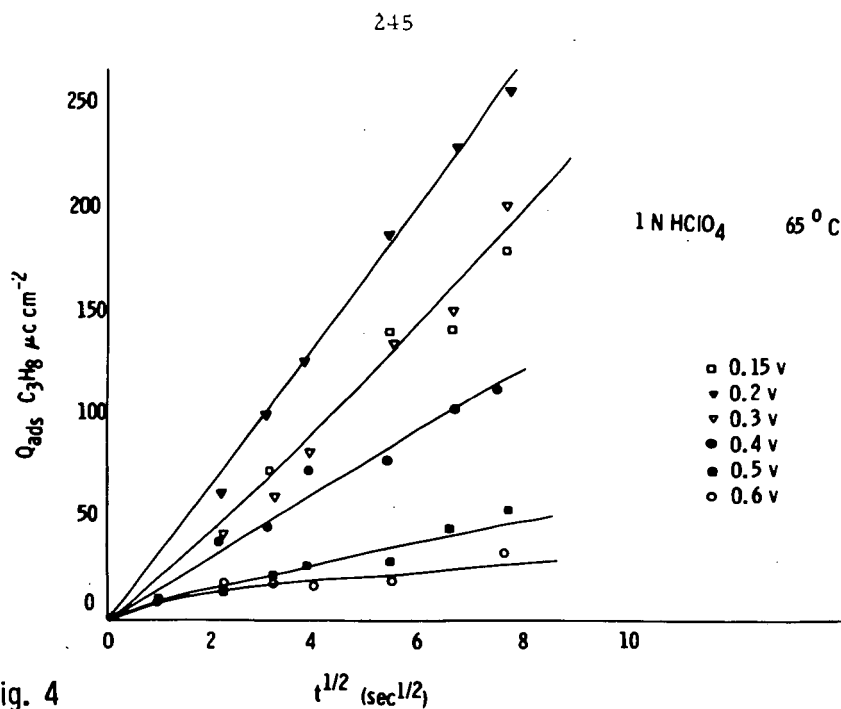


Fig. 4

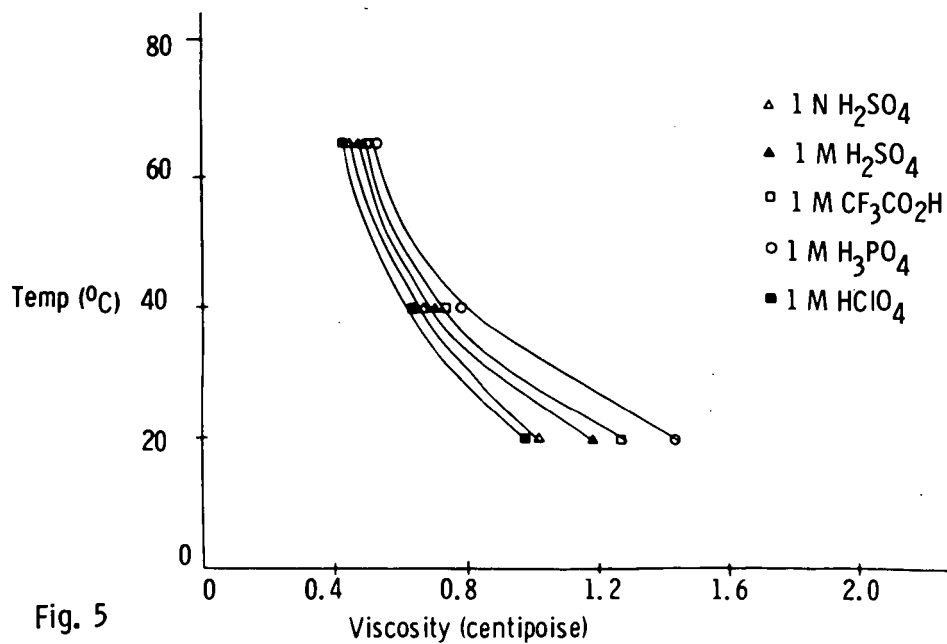


Fig. 5



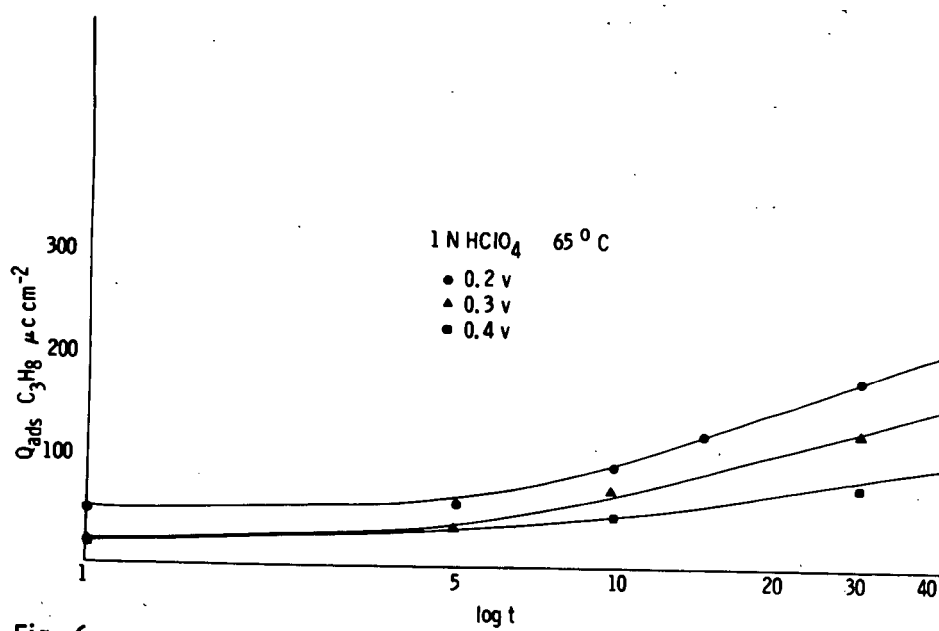


Fig. 6